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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA COMPUTER PROGRAM TGA--ETC(U)
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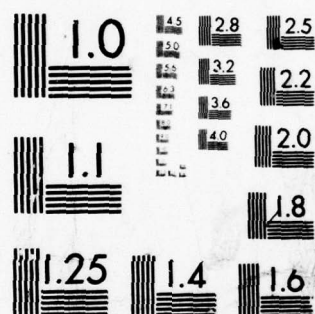AWRE-O-56/78   DRIC-BR-67686   NL
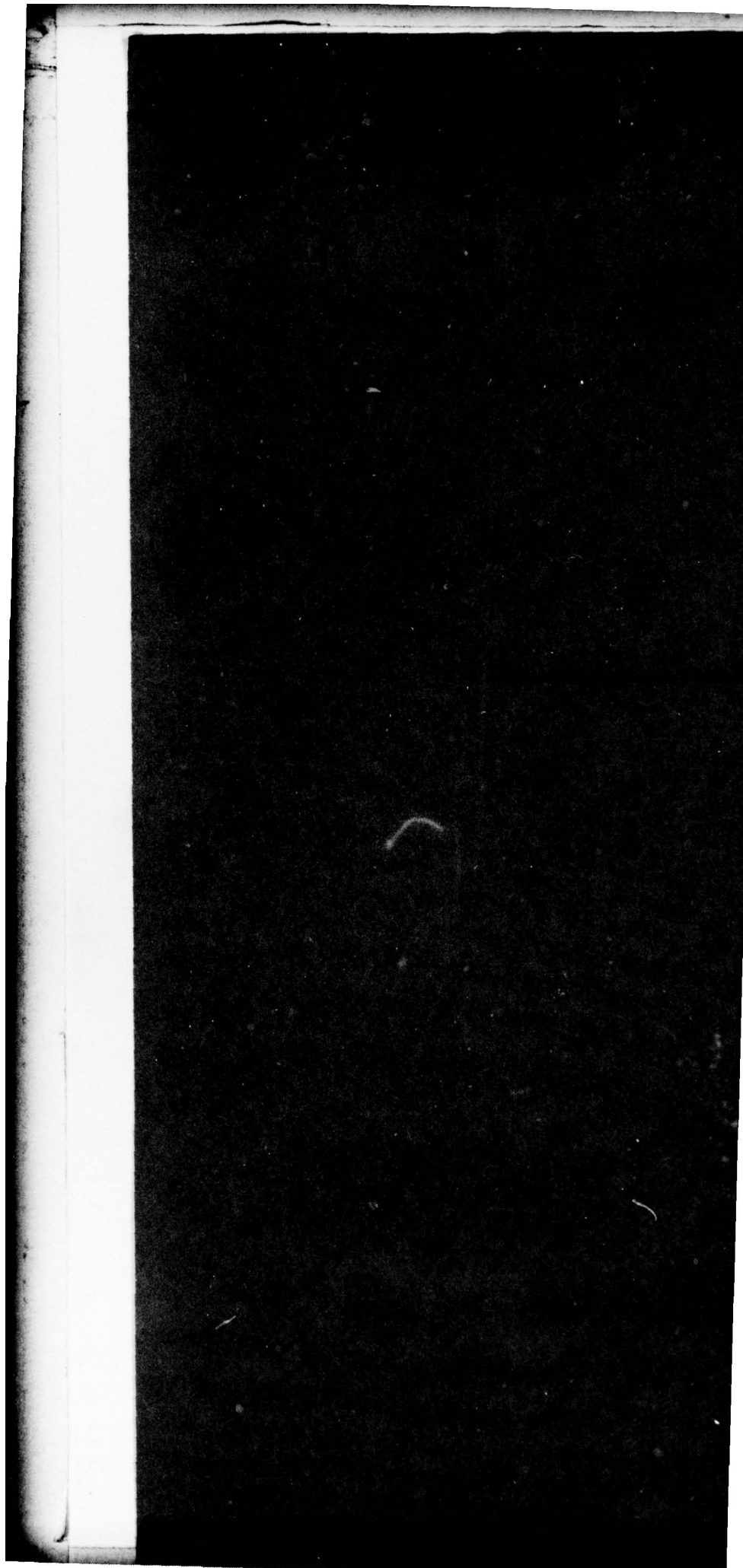
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(6) Kinetic Analysis of Thermogravimetric Data
Computer Program TGA2

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CONTENTS

SUMMARY

Zsako has modified a curve fitting method reported by Doyle and in this report the method is further simplified to allow the use of a digital computer. The best description of the thermogram step was found to be given by 19 equally spaced co-ordinates between the $(1 - \alpha)$ limits of 0.05 to 0.95.

These co-ordinates, together with the heating rate, are used to calculate E and log Z, by an iterative process which minimises the standard deviation of the log $g(\alpha)$ − log $p(x)$ values.

The standard deviation allows a comparative assessment of the validity of the kinetic equations chosen to represent the mechanism of the reaction. A further simplification involved the use of an approximate equation for − log $p(x)$ in place of tabulated values.

The TGA2 method of calculation was shown to be valid by re-calculating E and log Z for standard curves which were generated from tables of − log $p(x)$.

Published data by Doyle and Zsako were re-calculated and the answers were in good agreement with the original results.

1.   INTRODUCTION

The thermal decomposition of solids may be described by the equation $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$.

This is a simplified statement of a complex process in which many different steps may be proceeding simultaneously. These include physical processes such as diffusion of heat and diffusion of gaseous products, as well as breaking of chemical bonds.

Thus, the kinetics of thermal decomposition reactions depend upon experimental conditions as well as the chemical nature of the solid [1,2].

Many efforts have been made to obtain kinetic parameters from isothermal and dynamic thermograms and these have been reviewed [3,4].

Utilising a single weight loss/temperature curve has an obvious advantage over isothermal weight loss/time curves produced at several different temperatures. Graphical comparison methods have been used [5] but if TGA data can be prepared in a suitable form, the computer can remove most of the tedium and cost of the calculation.

A suitable method for this kind of treatment was a curve fitting method reported by Doyle [6] and later simplified by Zsako [7]. This report describes how the method was further simplified to allow the required parameters to be extracted quickly while retaining the accuracy of the original method.

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The usual notations were used, ie:-

α = fractional weight loss,

E = activation energy in kcal/mole,

Z = pre-exponential factor,

b = order of reaction,

R = gas constant,

$S^{\ddagger}$ = activation entropy,

h = Planck's constant,

k = Boltzmann's constant,

$T_{\frac{1}{2}}$ = temperature of half weight loss,

u = E/RT,

x = the value of u at the sample temperature.

2.   THE DOYLE/ZSAKO METHOD

2.1   The outline of the method

The equation to a thermogram is

$$g(\alpha) = \frac{ZE}{Rq}p(x), \qquad \qquad \ldots\ldots(1)$$

where the form of $g(\alpha)$ depends upon the nature of the process and

$$p(x) = \frac{e^{-x}}{x} - \int_{x}^{\infty} \frac{e^{-u}}{u}.du. \qquad \ldots\ldots(2)$$

Doyle prepared a table of $-\log p(x)$ from x = 10 to x = 50. A first approximation of E was calculated assuming the reaction order to be unity, and this approximation was improved by trial and error curve fitting techniques. Zsako simplified this process as follows. Taking logs and rearranging, equation (1) becomes

$$\log \frac{ZE}{Rq} = \log g(\alpha) - \log p(x) = B, \qquad \ldots\ldots(3)$$

where B is dependent upon the nature of the compound and the heating rate but not upon the temperature.

The value of $g(\alpha)$ can be found for a given temperature if the particular function of α is known, and $-\log p(x)$ can be obtained from Doyle's tables if E is known.

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Then, if E is known and used to calculate B at several temperatures, the constancy of B will indicate the validity of the particular kinetic equation selected to calculate $g(\alpha)$. Conversely, if the kinetic equation representing the reaction is known, the constancy of B will indicate the validity of a chosen E value. The constancy of B can be quantified by means of the standard deviation,

$$\text{SIGMA} = \sqrt{\frac{\sum B^2 - \frac{(\sum B)^2}{N}}{N-1}}, \qquad \ldots\ldots(4)$$

where N is the number of B values. $(\text{SIGMA})_{\min}$ will indicate which of two E values (or which of two kinetic equations) best fits the reaction.

Taking the form of the kinetic equation as $f(\alpha) = (1 - \alpha)^b$, Zsako assumed, in turn, reaction orders of 0, 1/3, 1/2, 2/3, 1 and 2 and found a value for E, in each case, which gave a minimum standard deviation of B values. Comparing the $(\text{SIGMA})_{\min}$ values corresponding to the six E values, the overall $(\text{SIGMA})_{\min}$ value indicated which of the six kinetic equations best fitted the reaction.

The six kinetic equations are listed in table 1.

TABLE 1

Kinetic Equations Based on $f(\alpha) = (1 - \alpha)^b$ [7]

b	Form of $g(\alpha)$
0	(α)
$\frac{1}{3}$	$\frac{3}{2}\left[1 - \sqrt[3]{(1 - \alpha)^2}\right]$
$\frac{1}{2}$	$2\left[1 - \sqrt{(1 - \alpha)}\right]$
$\frac{2}{3}$	$3\left[1 - \sqrt[3]{(1 - \alpha)}\right]$
1	$-\ln(1 - \alpha)$
2	$\frac{\alpha}{1 - \alpha}$

If the selected $(\text{SIGMA})_{\min}$ value is small enough, $\bar{B}$ can be used to calculate Z from equation (3).

Then $\bar{B} = \log ZE/Rq$ and

$$\log Z = \bar{B} + \log Rq - \log E, \qquad \ldots\ldots(5)$$

also the apparent activation entropy

$$S^{\ddagger} = 2.303R \log \frac{ZH}{kT_{\frac{1}{2}}}. \qquad \ldots\ldots(6)$$

In order to extend Doyle's tabulated $- \log p(x)$ values when $x > 50$ Zsako used the approximation

$$p(x) = e^{-x}(\frac{1}{x^2} - \frac{2}{x^3}) \qquad \ldots\ldots(7)$$

and intermediate values of $- \log p(x)$ were found by interpolation.

2.2   **Modification of the Doyle/Zsako method for TGA2**

2.2.1   **Calculation of $- \log p(x)$**

Comparing the approximation equation (7) with values for x obtained from standard tables of e^{-x} and the integral

$$\int_{x}^{\infty} \frac{e^{-u}}{u} du,$$

it was shown (table 2) that the approximation is sufficiently close down to $x = 4.0$. Then, instead of using tables of $- \log p(x)$, equation (7) was used throughout this work. In practice x is rarely less than 4.0, but in the event, a diagnostic message was printed by the computer program to indicate that E was inaccurate.

TABLE 2

A Test of the Approximation Equation (7)
over the Range x = 2 to 50

x	A $- \log p(x)$ from Integral (Tabulated Values)[8]	B $- \log p(x)$ from Approximation Equation (7)	Ratio B/A
50	25.129	25.125865	0.99988
40	20.597	20.594464	0.99988
30	16.010	16.010155	1.0000
20	11.328	11.331665	1.0003
10	6.415666	6.438694	1.00359
9	5.896899	5.925212	1.00480
8	5.368888	5.404500	1.00663
7	4.829246	4.875506	1.00958
6	4.274602	4.337379	1.01469
5	3.699839	3.790578	1.02453
4	3.096592	3.241743	1.04687
3	2.449659	2.733754	1.11597
2	1.726291	16.882666	9.780

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3.   DESCRIPTION OF THE PROGRAM TGA2

TGA2 is written in FORTRAN and has been successfully used for
several years, and recently on the IBM 370/168. It is described under the
headings Input, Program and Output, in sections 3.1 to 3.3. A thermogram
may consist of one or more steps which represent different reactions and
these steps must be treated separately. The data for a weight loss step
were plotted as active weight fractions $(1 - \alpha)$, as a function of temperature
and a smooth curve was drawn using a flex rule. It was the position on the
temperature scale and the shape of this smoothed curve which was used as
a basis for the calculation of kinetic parameters. Values of temperature
were taken from the smoothed curve corresponding to equal increments of
$(1 - \alpha)$ and an example is given in figure 1 where 19 co-ordinates were
taken corresponding to $(1 - \alpha)$ values from 0.05 to 0.95 in equal
increments of 0.05. The extremes of the curve, ie, $(1 - \alpha) = 1.0$ and 0.0
were not used because of the inaccuracy of estimating temperature at small
slopes.

3.1   Input

Line Number	Format	Symbol	Explanation
1	I2	NDATA	The number of pairs of co-ordinates describing the smoothed curve
2	F6.3	HDIF	Increments of $(1 - \alpha)$
3	6A4	ORDER(J)	Titles for the different kinetic equations
4 to (NDATA + 4)	F7.4	H(I)	Active weight fractions $(1 - \alpha)$
NDATA + 5	I8	RUN	Run identity number
	A8	STEP	Step identity number
	A8	RANGE	Temperature limits of step in °C
	F8.3	QM	Heating rate °C/min
NDATA + 6 to (2 NDATA + 6)	F7.1	TC(I)	Temperature in °C corresponding to the active weight fractions on line 4 onwards
Last line	–	–	Blank

Note that several sets of data may be calculated in one
computer run, additional sets corresponding to lines (NDATA + 5) to
(2NDATA + 6) being stacked together without spaces. In all cases the
last line of the complete data input must be blank. All data sets applied
at one time must be compatible with the lines 1 to (NDATA + 4) which are
not repeated.

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3.2   Program TGA2

A flow chart showing the logic of TGA2 is shown in figure 5 and a full print-out of the FORTRAN statements is reproduced in appendix A. The main calculations embodied in TGA2 are explained in sections 3.2.1 to 3.2.3.

3.2.1   Minimum of SIGMA (equation (4))

At a constant heating rate, SIGMA is a function dependent on activation energy. Then, for a given rate equation, $g(\alpha)$, SIGMA may be minimised by finding the appropriate value for E. Subroutine VD01A [9] finds the minimum of a function of a single variable by an iterative process. In this case the variable is E and the function is

$$\sqrt{\frac{\Sigma B^2 - \frac{(\Sigma B)^2}{N}}{N - 1}} .$$

The subroutine requires a starting approximation of E and this is provided by

$$E_{(approx)} = \frac{- RT^2}{- \ln(1 - \alpha)} \cdot \frac{d(1 - \alpha)}{dT}$$ (cf, reference [10],

equation 21)   .....(8)

The iterative process continued until E is precise to within 25 cal/mole.

3.2.2   Calculation of $\frac{d(1 - \alpha)}{dT}$

Subroutine SLOPE calculates the slope of a curve from a list of co-ordinates using the Newton-Stirling [11] formula for central differences when the argument changes by a fixed amount (HDIF in this subroutine). The slope at $(1 - \alpha) = 0.8$ is used in equation (8) to calculate $E_{(approx)}$.

3.2.3   Diagnostics

If E/RT is allowed to assume a value ≤ 2.0, the program will stop at Statement 117 having tried to find the log of a negative number. To avoid this during the iterative process, a barrier has been inserted (Statement 109) so that, if E/RT ≤ 2.1, SIGMA is put to 1000.0 to change the direction of search for $SIGMA_{min}$.

If E/RT is < 4.0 for $SIGMA_{min}$, table 2 shows that E will be inaccurate and in the event a statement is printed to that effect.

If the number of evaluations of SIGMA exceeds the limit stated when VD01A is called (100 in TGA2) then a diagnostic is printed – "MAXFUN TOO SMALL".

A diagnostic message will be printed if ROUNDING ERRORS prevent the calculation of E to the desired precision.

3.3 Output

The output from TGA2 is in the form of a table and an example is given in figure 2. This table lists $SIGMA_{min}$ and the corresponding calculated values for activation energy, $log Z$, Z and activation entropy ($S^{\ddagger}$). Each line represents a different $g(\alpha)$ function and the best values are those in line with the minimum $SIGMA_{min}$ (sic) value.

Points to note are:-

(a) The calculation will indicate the best fit to the data of the $g(\alpha)$ functions included in the program. If the correct $g(\alpha)$ function is not included, a misleading answer will be given.

(b) Log Z and S are calculated in all cases, but these are valid only if $SIGMA_{min}$ is sufficiently small.

4. DESCRIPTION OF THE CURVE

The basis for the calculation of kinetic parameters by TGA2 was a description of the smoothed thermogram step in terms of the co-ordinates $(1 - \alpha)$ and T. There were possible variations in this description, such as range and number of co-ordinates, which would possibly affect the results of the calculation. These variations were investigated as follows:-

(a) The effect of limiting the range of $(1 - \alpha)$ by truncating both ends of the curve simultaneously (section 4.2).

(b) The effect of limiting the number of co-ordinates, uniformly spaced with respect to $(1 - \alpha)$ (section 4.3).

(c) The effect of truncating the ends of the curve separately (section 4.4).

(d) With a $(1 - \alpha)$ spacing of 0.05 (19 co-ordinates) the effect of taking the top 7, middle 7 and bottom 7 co-ordinates in turn (section 4.5).

In order to make a quantitative assessment of the various treatments discussed in sections 4.2 to 4.5, standard thermograms were required with known kinetic parameters. These were calculated from assumed values of the relevant kinetic parameters and the equation to the thermogram (equation (1)). They covered the range of activation energies which were likely to be encountered in thermal degradation reactions, ie, from 10 to 66 kcal/mole (section 4.1).

It can be seen from the results of the investigations into the description of the curves in tables 5, 6 and 7 that the values of E and log Z are not greatly affected by the variations applied and, therefore, a different quantitative assessment was devised depending upon the SIGMA values. It may be said that the choice of best SIGMA is easier and probably more reliable if it is much smaller than the next best value of SIGMA, or, in other words, if the ratio (next best SIGMA/best SIGMA) is large. The value of this ratio has been used thoughout this work as a criterion when judging between the different treatments applied to the standard curves.

4.1   Preparation of four standard curves

TABLE 3

Assumed Kinetic Parameters for the Standard Thermograms

E, kcal/mole	Log Z	Reaction Order (b)	Heating Rate, q, °C/min
10.0	2.4	1	10
30.0	10.0	1	10
50.0	15.0	1	10
66.0	19.0	1	10

The values shown in table 3 were substituted in a rearranged equation (1) when $g(\alpha) = (1 - \alpha)^b$, ie,

$$(1 - \alpha)^b = \frac{ZE}{Rq} \, p(x),$$

and using Zsako's tables for $- \log p(x)$ at different temperatures, several $(1 - \alpha)$ and T co-ordinates were calculated and used as a basis for four standard curves. The curves were smoothed and initially described by 33 co-ordinates with a range of $(1 - \alpha)$ from 0.02 to 0.98 in equal steps of 0.03. These are reproduced in table 4.

TABLE 4

Co-ordinates Taken from Four Smoothed Standard Curves

(a) E = 10.0 log Z = 2.4   (b) E = 30.0 log Z = 10.0
(c) E = 50.0 log Z = 15.0   (d) E = 66.0 log Z = 19.0

(1 − α)	Temperature, °C			
	(a) $10/10^{2.4}$	(b) $30/10^{10}$	(c) $50/10^{15}$	(d) $66/10^{19}$
0.98	80.0*	208.5	314.2	367.0
0.95	100.0	221.6	327.3	377.9
0.92	112.3	229.3	334.4	384.0
0.89	121.3	234.5	339.1	388.2
0.86	128.5	238.8	342.6	391.4
0.83	134.3	242.5	345.6	394.0
0.80	139.4	245.5	348.2	396.5
0.77	144.3	248.2	350.4	398.6
0.74	148.6	250.5	352.5	400.4
0.71	152.7	252.4	354.4	402.1
0.68	156.3	254.3	356.2	403.6
0.65	159.6	256.1	357.8	405.1
0.62	162.9	257.9	359.5	406.5
0.59	166.2	259.7	360.8	407.9
0.56	169.4	261.5	362.1	409.3
0.53	172.5	263.2	363.6	410.5
0.50	175.5	264.7	365.1	411.7
0.47	178.6	266.2	366.5	412.9
0.44	181.5	267.8	367.8	414.0
0.41	184.4	269.3	369.0	415.0
0.38	187.4	270.9	370.3	416.2
0.35	190.3	272.4	371.5	417.3
0.32	193.2	273.9	372.6	418.5
0.29	196.2	275.3	373.8	419.7
0.26	199.4	276.8	375.1	420.9
0.23	202.7	278.5	376.5	422.3
0.20	206.2	280.2	378.0	423.5
0.17	210.0	282.0	379.7	424.9
0.14	214.1	284.1	381.5	426.4
0.11	219.0	286.5	383.5	427.8
0.08	224.5	289.2	385.7	429.5
0.05	231.4*	292.5	388.3	431.6*
0.02	245.2*	298.0	392.8	435.3*

*Calculated from $p(x) = e^{-x}(\frac{1}{x^2} - \frac{2}{x^3})$.

4.2   <u>The effect of limiting the range of (1 - α) by truncating</u>
         <u>the ends of the curve</u>

         Table 5 shows that the re-calculated values for E and log Z
are altered little by this treatment of the standard curves, and they
are at worst within a few per cent of those assumed. The lowest range,
0.2/0.8, shows a low value for the ratio (next best/best SIGMA) in all
four cases and this shows that the ends of the curve beyond 0.2/0.8 are
necessary if the correct or minimum SIGMA value is to be distinguished
easily. On balance the range 0.05/0.95 is to be preferred with
two instances of the highest ratio favouring this range.

TABLE 5

<u>The Effect of Limiting the Range of (1 - α) Values</u>
<u>Using Co-ordinates from the Standard Thermograms</u>

E/Log Z	Range	NDATA*	E	Log Z	Best SIGMA	Next Best SIGMA	Ratio Next Best SIGMA/Best
10/2.4	0.02/0.98	33	10.1	2.5	0.00580	0.0355	6.12
	0.05/0.95	31	10.0	2.4	0.00187	0.0224	11.98
	0.08/0.92	29	10.0	2.4	0.00167	0.0176	10.54
	0.20/0.80	21	10.1	2.4	0.00152	0.00693	4.56
30/10.0	0.02/0.98	33	30.1	10.0	0.00525	0.0353	6.72
	0.05/0.95	31	30.0	10.0	0.00452	0.0244	5.4
	0.08/0.92	29	30.0	10.0	0.00446	0.0194	4.35
	0.20/0.80	21	30.1	10.1	0.00429	0.00947	2.21
50/15.0	0.02/0.98	33	50.2	15.1	0.00624	0.0320	5.13
	0.05/0.95	31	50.4	15.1	0.00468	0.0250	5.34
	0.08/0.92	29	50.6	15.2	0.00419	0.0198	4.73
	0.20/0.80	21	50.7	15.2	0.00355	0.00624	1.76
66/19.0	0.02/0.98	33	66.0	19.0	0.00633	0.0312	4.93
	0.05/0.95	31	65.7	18.9	0.00486	0.0222	4.57
	0.08/0.92	29	65.5	18.8	0.00356	0.0182	5.11
	0.20/0.80	21	65.2	18.7	0.00248	0.00829	3.34

Note: In all cases the best fit was given with b = 1.
*Number of co-ordinates.

4.3   <u>The effect of limiting the number of uniformly spaced (1 - α)</u>
         <u>values in the range 0.05 to 0.95</u>

         Again the recalculated E and log Z values vary little with the
different treatments.

Comparing the recalculated values of E and log Z in table 6 with the assumed values, the smallest NDATA is marginally favoured. The ratio (next best/best SIGMA) suggests that the best distinction is obtained at either NDATA = 7 or 19.

TABLE 6

The Effect of Limiting the Number* of Uniformly Spaced $(1 - \alpha)$ Values

E/Log Z	$(1 - \alpha)$ Limits	(NDATA)*	$(1 - \alpha)$ Spacing (HDIF)	E	Log Z	Best SIGMA	Next Best SIGMA	Ratio Next Best SIGMA/Best
10/2.4	0.05/0.95	31	0.03	10.0	2.4	0.00187	0.0224	12.0
		19	0.05	10.0	2.4	0.00219	0.0243	11.1
		7	0.15	10.0	2.4	0.00165	0.0329	19.9
30/10.0	0.05/0.95	31	0.03	30.0	10.0	0.00452	0.0244	5.4
		19	0.05	29.9	10.0	0.00375	0.0259	6.91
		7	0.15	29.9	10.0	0.00521	0.0353	6.78
50/15.0	0.05/0.95	31	0.03	50.4	15.1	0.00468	0.0250	5.3
		19	0.05	50.4	15.1	0.00278	0.0254	9.1
		7	0.15	50.3	15.1	0.00309	0.0335	10.8
66/19.0	0.05/0.95	31	0.03	65.7	18.9	0.00486	0.0222	4.4
		19	0.05	65.8	18.9	0.00520	0.0240	4.6
		7	0.15	66.1	19.0	0.00676	0.0306	4.5

*Number of co-ordinates.

4.4   The effect of progressive removal of the ends of the curve

Figures 3 and 4 show a similar effect and there is a downward trend in the ratio (next best/best SIGMA) as the end of the curve is reduced. The maximum at 0.05 and 0.95 in some cases suggests that the co-ordinates at the extremes of the curve, ie, 0.02 and 0.98, are not always reliable. Limits of 0.05 and 0.95 are favoured on balance.

4.5   The relative importance of the different parts of the $(1 - \alpha)$/T curve

Taking a curve represented by 19 co-ordinates with a $(1 - \alpha)$ spacing of 0.05, the re-calculated results from the whole curve is compared in table 7 with the re-calculated values from the top, middle and bottom parts of the curve respectively. Surprisingly, the E and log Z values do not vary much, except in the case of the bottom part of the 66/19.0 curve. The list of ratios (next best/best SIGMA) shows that, as far as distinguishing one SIGMA from another, the middle and the top parts of the curve were poor, with an improvement shown from the bottom part of the curve which was, therefore, judged to be the most important part for this purpose.

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TABLE 7

The Relative Importance of the Different Parts of the (1 − α)/T Curve with all (1 − α) Spacings of 0.05

E/Log Z	(1 − α) Limits	Part of Curve	Order	E	Log Z	Best SIGMA	Next Best SIGMA	Ratio Next Best SIGMA/Best
10/2.4	0.05/0.95	Whole	1	10.0	2.4	0.00219	0.0243	11.1
	0.05/0.35	Bottom	1	10.1	2.5	0.00138	0.00594	4.3
	0.35/0.65	Middle	1	10.0	2.4	0.000475	0.00193	4.1
	0.65/0.95	Top	2/3	9.7	2.2	0.00253	0.00261	1.0
30/10.0	0.05/0.95	Whole	1	29.9	10.0	0.00375	0.0259	6.9
		Bottom	1	29.8	9.9	0.00197	0.00726	3.7
		Middle	1	29.9	9.7	0.00115	0.00142	1.2
		Top	$\frac{1}{2}$	28.7	9.4	0.00188	0.00208	1.1
50/15.0	0.05/0.95	Whole	1	50.4	15.1	0.00278	0.0254	9.1
		Bottom	1	50.2	15.1	0.00254	0.00740	2.9
		Middle	1	50.2	15.1	0.00238	0.00331	1.4
		Top	2/3	48.8	14.5	0.00171	0.00240	1.4
66/19.0	0.05/0.95	Whole	1	65.8	18.9	0.00520	0.0240	4.6
		Bottom	2/3	48.7	13.3	0.00126	0.00383	3.0
		Middle	2/3	57.6	16.2	0.00158	0.00189	1.2
		Top	1	66.2	19.1	0.00216	0.00323	1.5

5. DISCUSSION

The aim in writing TGA2 was to provide the means of calculating kinetic parameters from dynamic thermogravimetric data, and to do it easily and quickly, and for the results to be at least as reliable as other available methods.

Doyle [6] has provided adequate thermogravimetric data on octamethylcyclotetrasiloxane (OMCTS) and polytetrafluoroethylene (PTFE). The relevant numbers (19 temperatures and 1 heating rate for each run) were abstracted from the paper and applied to the computer with program TGA2. The process for both sets took approximately 30 min plus a few seconds computer time. A comparison of the results is shown in table 8.

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TABLE 8

A Comparison of Results from Reference [6] and TGA2

Method	OMCTS		PTFE	
	Activation Energy, kcal/mole	Order	Activation Energy, kcal/mole	Order
Ref [6]	11.65	0	66-68	1
TGA2	11.44	0	60.45	2/3

Zsako has published data [7] from the thermal decomposition of
(I) $Co(dimethylglyoxime)_2(p.ethylaniline)_2NCS$ and (II) $Co(dimethylglyoxime)_2$
$(\gamma-picoline)_2NCS$. He has calculated kinetic parameters for the decomposition
of these compounds using the Horowitz and Metzger method, the Freeman and
Carroll method, as well as the modified Doyle method. These results are
compared with TGA2 in table 9.

TABLE 9

A Comparison of Kinetic Parameters Calculated for Cobalt Complexes I and II by Different Methods

Method	Compound I				Compound II			
	E	Reaction Order	Z	$S^{\ddagger}$	E	Reaction Order	Z	$S^{\ddagger}$
Horowitz and Metzger	42	2	–	–	33	1	–	+ 1
Zsako	28.9	1	11.71	– 5.84	28.3	1	11.45	– 7.06
Freeman and Carroll	29.2	1.16	–	–	28.7	0.82	–	–
TGA2	27.7	1	10.77	– 10.16	28.5	1	11.12	– 8.54

Both tables 8 and 9 indicate that the TGA2 results are comparable
with the original results of Doyle, Zsako and with those of Freeman and
Carroll. All of these give a lower value for activation energy than the
Horowitz and Metzger method.

A word of warning is probably necessary at this stage.

The method of using TGA2 is so simple that there is a
temptation to do the calculations and quote values for kinetic parameters
which are meaningless, and it is especially important to remember the
limitations of the method; the important ones are listed as follows:-

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(a) The weight loss step which is considered must be directly related to a simple reaction and not compounded from several different processes.

(b) The results will only be as good as the original TGA experimental results allow.

For instance, care must be taken to minimise diffusion effects which arise from the use of samples with a large particle size, or a high heating rate. Particular attention should be paid to the lower 1/3 or "tail" of the curve which has been shown to be distinctive. Also in this area, a build-up of non-volatile catalysts as the weight loss proceeds may cause spurious results, eg, impure carbon burning in air.

(c) The third important consideration is to decide which mechanism best describes the solid state reaction. Zsako has used the six relatively simple equations listed in table 1, but many others have been developed and they are designed to accommodate different rate controlling processes. Examples are given in table 10.

TABLE 10

Kinetic Equations Based on Various Solid State Mechanisms [8]

Function	Equation	Rate-Controlling Process
D_1	$\alpha^2 = kt$	One-dimensional diffusion
D_2	$(1 - \alpha) \ln (1 - \alpha) + \alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D_3	$[1 - \sqrt[3]{1 - \alpha}]^2 = kt$	Three-dimensional diffusion, spherical symmetry; Jander equation
D_4	$(1 - \frac{2}{3}\alpha) - \sqrt[3]{(1 - \alpha)^2} = kt$	Three-dimensional diffusion, spherical symmetry; Ginstling-Brounshtein equation
F_1	$- \ln (1 - \alpha) = kt$	Random nucleation, one nucleus on each particle
A_2	$\sqrt{- \ln (1 - \alpha)} = kt$	Random nucleation; Avrami equation
A_3	$\sqrt[3]{- \ln (1 - \alpha)} = kt$	Random nucleation; Avrami equation
R_2	$1 - \sqrt{1 - \alpha} = kt$	Phase boundary reaction, cylindrical symmetry
R_3	$1 - \sqrt[3]{1 - \alpha} = kt$	Phase boundary reaction, spherical symmetry

Notable methods of calculating kinetic paramaters from thermal analysis curves have been developed by Freeman and Carroll [12], Coates and Redfern [13], Ozawa [14] and Sharp and Wentworth [15]. These have been compared by Ozawa [16].

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APPENDIX A

PROGRAM TGA2

```fortran
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION B(15,50)
      DIMENSION DTDH(50)
      DIMENSION EART(50)
      DIMENSION G(15,50)
      DIMENSION H(50)
      DIMENSION ORDER(15)
      DIMENSION PX(50)
      DIMENSION T(50)
      DIMENSION TC(50)
C
      PLANCK=6.624E-27
      BOLTZ=1.380E-16
      R=1.987DO
      READ(5,10) NDATA
   10 FORMAT(I2)
      READ(5,15) HDIF
   15 FORMAT(F6.3)
      READ(5,16) (ORDER(J),J=1,15)
   16 FORMAT(15A4)
      READ(5,20) (H(I),I=1,NDATA)
   20 FORMAT(F7.4)
  100 READ(5,8)IRUN,STEP,RANGE,QM
    8 FORMAT(I8,2A8,F8.3)
      Q=QM/60.
      IF(IRUN)_01,101,102
  101 STOP
  102 READ(5,21) (TC(I),I=1,NDATA)
   21 FORMAT(F7.1)
      DO 22 I=1,NDATA
      T(I)=TC(I)+273.2DO
   22 CONTINUE
      CALL SLOPE(T,NDATA,HDIF,DTDH)
      DHDT=1./DTDH(1)
      WRITE(6,9)IRUN,STEP,RANGE,NDATA,QM
    9 FORMAT('1','RUN',I8,2A8,4X,'NDATA=',I2,4X,'HEATING RATE =',F8.3,'D
     1EG.C.PER MIN.'//)
      L=(NDATA+1)/2
      WRITE(6,17) TC(L)
   17 FORMAT('  TEMPERATURE FOR HALF WEIGHT LOSS IN THIS STEP =',F7.1,2X
     1,'DEG.C.'/)
      EAPROX=(-R*(T(4)**2)*DHDT)/(-DLOG(H(4)))
      WRITE(6,18) H(4),DHDT
   18 FORMAT(' THE SLOPE DH/DT(AT H=',F7.4,') =',F12.2/)
      WRITE(6,19) EAPROX
   19 FORMAT(' A ROUGH ESTIMATE OF ACT.ENERGY =',-3PF10.2,'   KCAL/MOLE'
     1/)
      WRITE(6,11)
   11 FORMAT('  THE BEST FIT IS INDICATED BY THE MINIMUM SIGMA IN'/'  TH
     1E FOLLOWING TABLE SO USE THE VALUES IN THAT LINE.'//'  NOTE,THEY AR
     1E EMPIRICAL AND DEPEND ON THE EXPTL.METHOD.'//)
      WRITE(6,50)
   50 FORMAT(49X,'Z'/' REACTION',15X,'ACT.ENERGY',12X,'PRE EXP.',4X,'ACT
     1.ENTROPY'          /3X,'ORDER',7X,'SIGMA',3X,'(KCAL/MOLE)',4X,'LOG
     1 Z',4X,'FACTOR',3X,'(CAL/DEG.MOLE)'//)
```

```
      DO 55 J=1,6
      ITEST=2
    5 CALL V001AD(ITEST,EAPROX,F,100,25.0D0,0.0001D0,500.0D0)
      GO TO (1,2,3,4),ITEST
    1 DO 44 I=1,NDATA
  110 G(1,I)=1.-H(I)
  111 G(2,I)=3./2.*(1.-(H(I)**(2./3.)))
  112 G(3,I)=2.*(1.-DSQRT(H(I)))
  113 G(4,I)=3.*(1.-(H(I)**(1./3.)))
  114 G(5,I)=-DLOG(H(I))
  115 G(6,I)=(1.-H(I))/H(I)
  116 EART(I)=EAPROX/(R*T(I))
      IF(EART(I)-2.1D0)109,109,117
  109 F=1000.0D0
      GO TO 5
  117 PX(I)=DEXP(-EART(I))*((1./(EART(I)**2))-(2./(EART(I)**3)))
  118 B(J,I)=(DLOG(G(J,I))-DLOG(PX(I)))/2.303D0
   44 CONTINUE
      F=0.0D0
      FS=0.0D0
      DO 45 I=1,NDATA
  119 F=F+B(J,I)**2
  120 FS=FS+B(J,I)
   45 CONTINUE
      F=DSQRT((F-(FS**2)/FLOAT(NDATA))/FLOAT(NDATA-1))
      GO TO 5
    2 IF(EART(NDATA)-4.0D0)252,251,251
  251 BBAR=FS/FLOAT(NDATA)
      ZLOG=BBAR+DLOG(R*Q)/2.303D0-DLOG(EAPROX)/2.303D0
      Z=10.**ZLOG
      S=R*DLOG((Z*PLANCK)/(BOLTZ*T(L)))
      WRITE(6,60) ORDER(J),F,EAPROX,ZLOG,Z,S
   60 FORMAT(3X,A4,3X,E12.3,-3PF10.2,0PF10.2,E12.3,F13.2)
      GO TO 55
  252 WRITE(6,253) ORDER(J),F,EAPROX
  253 FORMAT(3X,A4,3X,E12.3,-3PF10.2,' CALCULATION INACCURATE AT THIS LO
     1W VALUE.')
      GO TO 55
    3 WRITE(6,65)
   65 FORMAT(20X,'ROUNDING ERRORS')
      GO TO 55
    4 WRITE(6,70)
   70 FORMAT(20X,'MAXFUN VALUE TOO SMALL'///)
   55 CONTINUE
      GO TO 100
      END
```

```
      SUBROUTINE SLOPE(Y,N,XDIF,DYDX)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DYDX(50)
      DIMENSION Y(50)
C
      DIMENSION DYF1(50)
      DIMENSION DYF2(50)
      DIMENSION DYF3(50)
      DIMENSION DYF4(50)
      DIMENSION DYF5(50)
      DIMENSION YMU1(50)
      DIMENSION YMU3(50)
      DIMENSION YMU5(50)
C
C
      NM1=N-1
      DO 5 I=1,NM1
      DYF1(I)=Y(I+1)-Y(I)
    5 CONTINUE
      NM2=N-2
      DO 10 I=1,NM2
      YMU1(I)=(DYF1(I)+DYF1(I+1))/2.
      DYF2(I)=DYF1(I+1)-DYF1(I)
   10 CONTINUE
      NM3=N-3
      DO 15 I=1,NM3
      DYF3(I)=DYF2(I+1)-DYF2(I)
   15 CONTINUE
      NM4=N-4
      DO 20 I=1,NM4
      YMU3(I)=(DYF3(I)+DYF3(I+1))/2.
      DYF4(I)=DYF3(I+1)-DYF3(I)
   20 CONTINUE
      NM5=N-5
      DO 30 I=1,NM5
      DYF5(I)=DYF4(I+1)-DYF4(I)
   30 CONTINUE
      NM6=N-6
      DO 35 I=1,NM6
      YMU5(I)=(DYF5(I)-DYF5(I+1))/2.
   35 CONTINUE
      DO 40 I=1,NM6
      DYDX(I)=(YMU1(I+2)-(YMU3(I+1)/6.)+(YMU5(I)/30.))/XDIF
   40 CONTINUE
      RETURN
      END
```
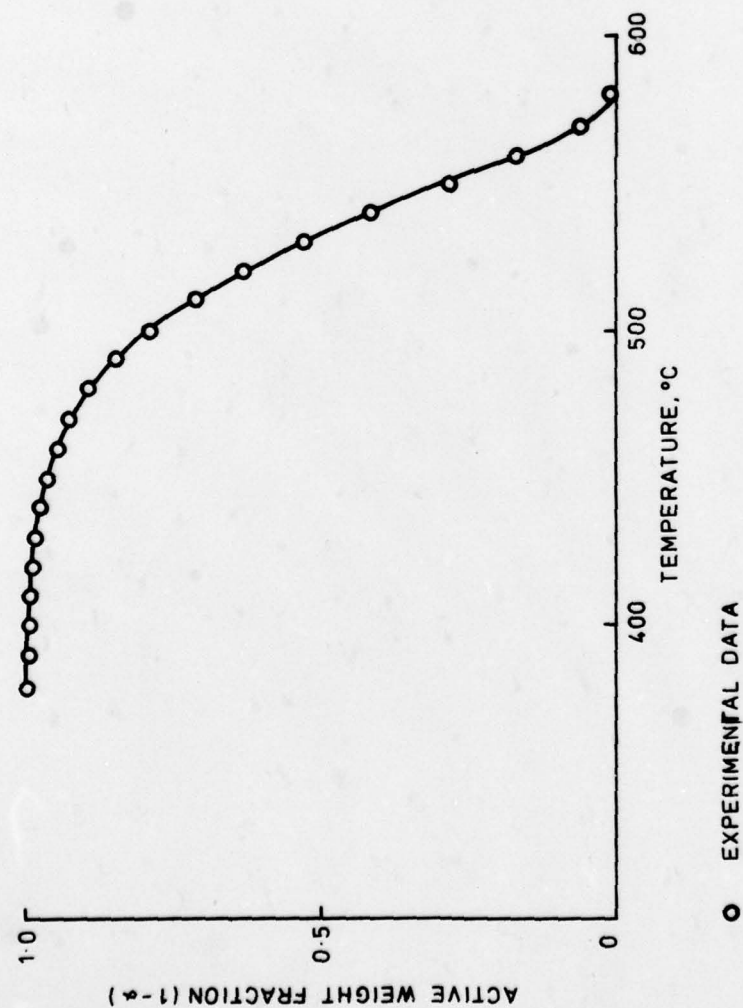
VALUES OF ACTIVE WEIGHT FRACTION
AND TEMPERATURE FROM
THE SMOOTHED CURVE

$(1-\alpha)$	$T°C$
0.95	458.0
0.90	478.0
0.85	489.5
0.80	499.0
0.75	506.5
0.70	512.5
0.65	518.0
0.60	523.5
0.55	528.5
0.50	533.0
0.45	537.0
0.40	541.0
0.35	545.0
0.30	548.5
0.25	552.0
0.20	556.0
0.15	560.5
0.10	565.0
0.05	571.0

ACTIVE WEIGHT FRACTION (1-α)

TEMPERATURE, °C

o   EXPERIMENTAL DATA

FIGURE 1   Smoothed $(1-\alpha)$ versus Temperature Plot for Run 73 Step 2

RUN 73 STEP2 380/580 NDATA=19 HEATING RATE = 0.685DEG.C.PER MIN.

TEMPERATURE FOR HALF WEIGHT LOSS IN THIS STEP = 533.0 DEG.C.

THE SLOPE DH/DT(AT H= 0.80000) = -0.58D-02
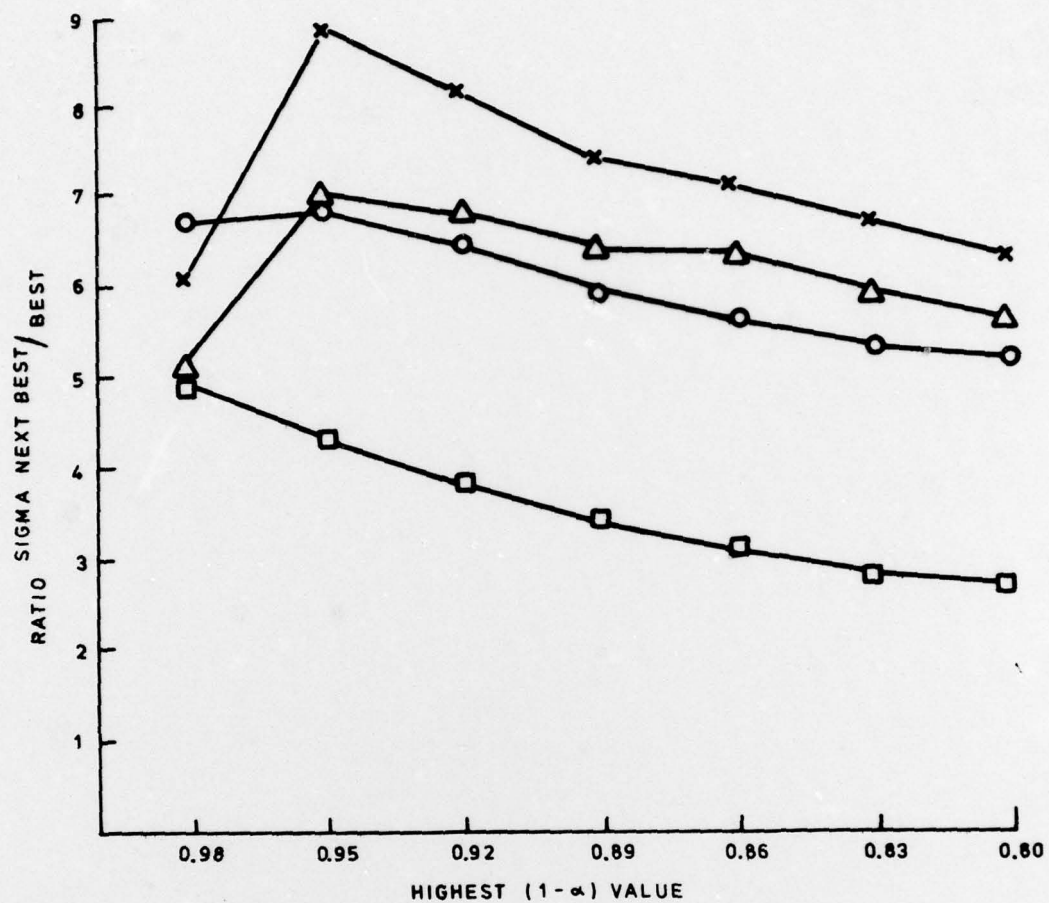
A ROUGH ESTIMATE OF ACT.ENERGY = 30.96 KCAL/MOLE

THE BEST FIT IS INDICATED BY THE MINIMUM SIGMA IN
THE FOLOWING TABLE SO USE THE VALUES IN THAT LINE.

NOTE,THEY ARE EMPIRICAL AND DEPEND ON THE EXPTL.METHOD.

REACTION ORDER	SIGMA	ACT.ENERGY (KCAL/MOLE)	LOG Z	PRE EXP. FACTOR Z	ACT.ENTROPY (CAL/DEG.MOLE)
ZERO	0.383D-01	29.26	4.07	0.117D 05	-41.90
1/3	0.222D-01	32.46	5.03	0.108D 06	-37.49
1/2	0.124D-01	34.24	5.57	0.371D 06	-35.03
2/3	0.445D-02	36.17	6.15	0.140D 07	-32.38
1	0.283D-01	40.44	7.42	0.265D 08	-26.55
2	0.150D 00	56.56	12.19	0.150D 13	-4.73

FIGURE 2 OUTPUT FROM PROGRAM TGA 2

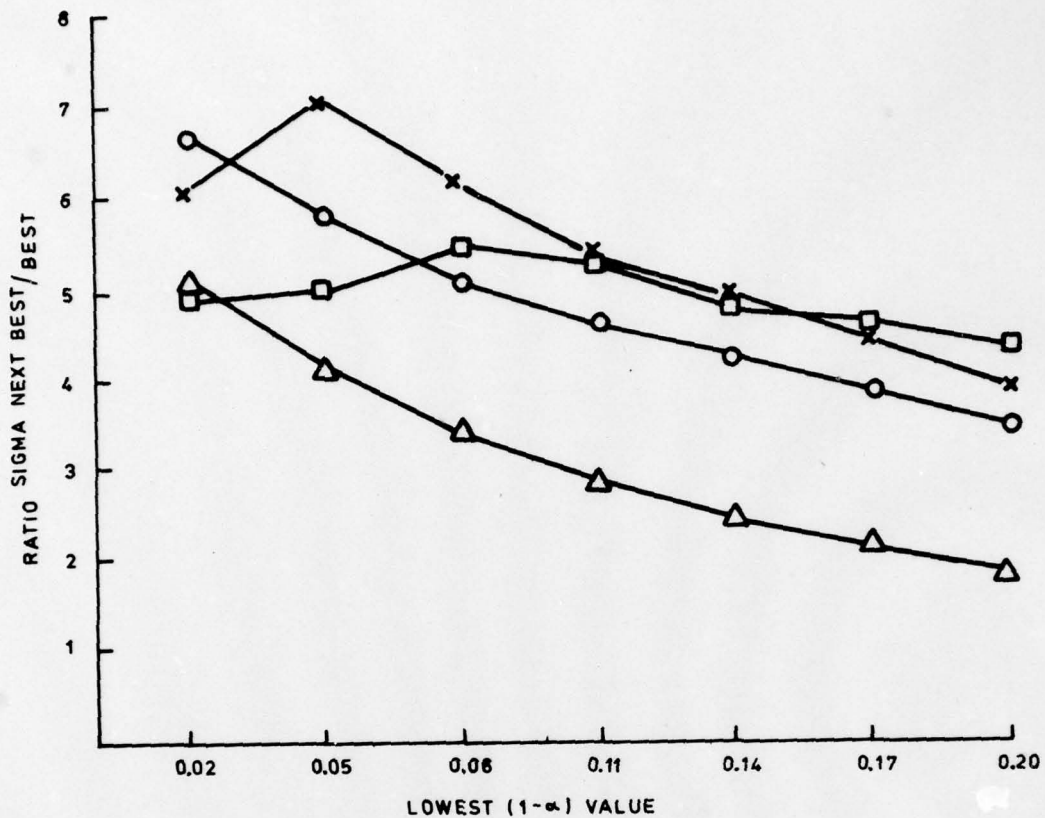FIGURE 3 Effect on Sigma Values of Progressive Removal
of Top of Standard Curve

FIGURE 4   Effect on Sigma Values of Progressive Removal
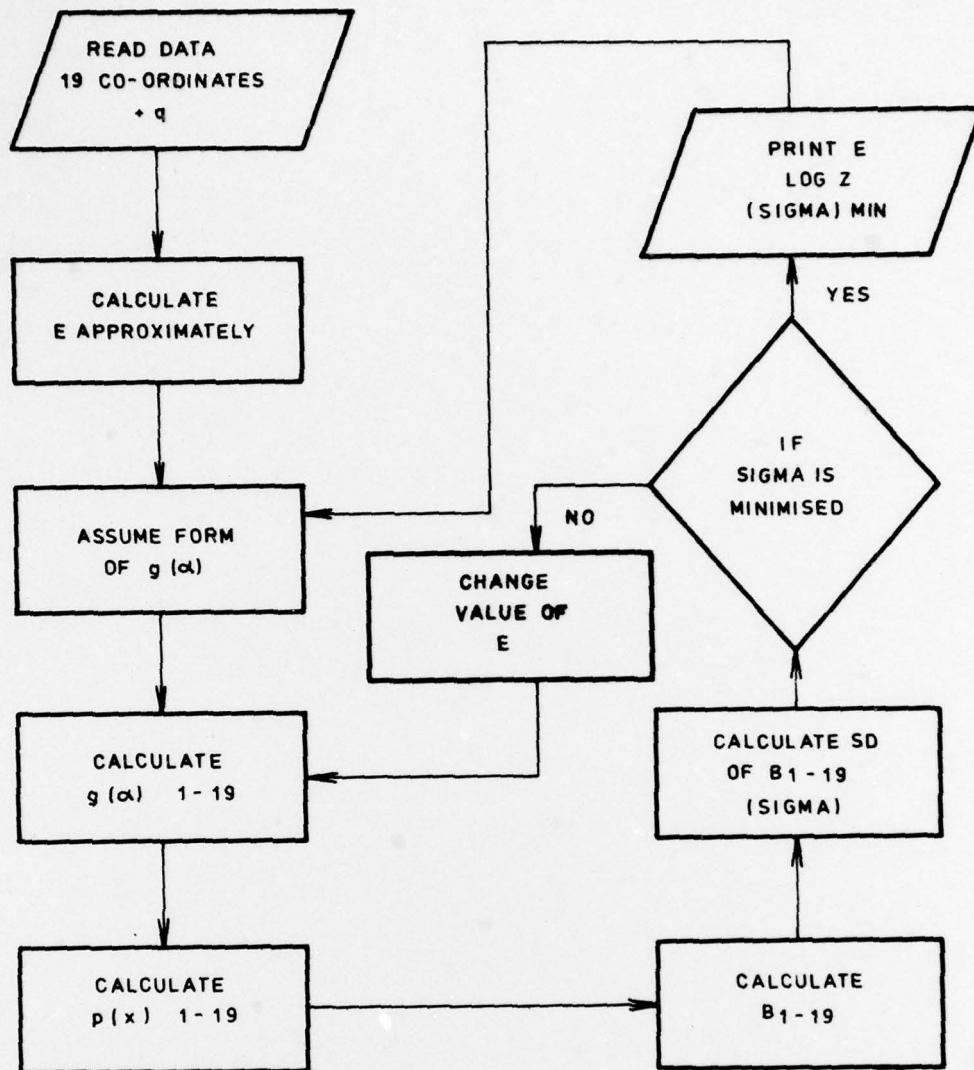of Bottom of Standard Curves

FIGURE 5   Simplified Flow Chart TGA2

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1. DRIC Reference (if known)	2. Originator's Reference	3. Agency Reference	4. Report Security Classification
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7a. Title in Foreign Language (in the case of Translation)

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7b. Presented at (for Conference Papers). Title, Place and Date of Conference

-

8. Author 1.Surname, Initials	9a. Author 2	9b. Authors 3, 4	10. Date	pp	ref
Briscall H	-	-	March 1979	26	16

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-	-	-	-

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Kinetics   Curve fitting
Thermogravimetry
Computer program TGA2

Abstract Zsako has modified a curve fitting method reported by Doyle and in this report the method is further simplified to allow the use of a digital computer. The best description of the thermogram step was found to be given by 19 equally spaced co-ordinates between the $(1 - \alpha)$ limits of 0.05 to 0.95. These co-ordinates, together with the heating rate, are used to calculate E and log Z, by an iterative process which minimises the standard deviation of the $\log g(\alpha) - \log p(x)$ values. The standard deviation allows a comparative assessment of the validity of the kinetic equations chosen to represent the mechanism of the reaction. A further simplification involved the use of an approximate equation for $- \log p(x)$ in place of tabulated values. The TGA2 method of calculation was shown to be valid by re-calculating E and log Z for standard curves which were generated from tables of $- \log p(x)$. Published data by Doyle and Zsako were re-calculated and the answers were in good agreement with the original results.

Some Metric and SI Unit Conversion Factors

(Based on DEF STAN 00-11/2 "Metric Units for Use by the Ministry of Defence",
DS Met 5501 "AWRE Metric Guide" and other British Standards)

Quantity	Unit	Symbol	Conversion
Basic Units			
Length	metre	m	1 m = 3.2808 ft
			1 ft = 0.3048 m
Mass	kilogram	kg	1 kg = 2.2046 lb
			1 lb = 0.45359237 kg
			1 ton = 1016.05 kg
Derived Units			
Force	newton	$N = kg\ m/s^2$	1 N = 0.2248 lbf
			1 lbf = 4.44822 N
Work, Energy, Quantity of Heat	joule	$J = N\ m$	1 J = 0.737562 ft lbf
			$1\ J = 9.47817 \times 10^{-4}$ Btu
			$1\ J = 2.38846 \times 10^{-4}$ kcal
			1 ft lbf = 1.35582 J
			1 Btu = 1055.06 J
			1 kcal = 4186.8 J
Power	watt	$W = J/s$	1 W = 0.238846 cal/s
			1 cal/s = 4.1868 W
Electric Charge	coulomb	$C = A\ s$	-
Electric Potential	volt	$V = W/A = J/C$	-
Electrical Capacitance	farad	$F = A\ s/V = C/V$	-
Electric Resistance	ohm	$\Omega = V/A$	-
Conductance	siemen	$S = 1\ \Omega^{-1}$	-
Magnetic Flux	weber	$Wb = V\ s$	-
Magnetic Flux Density	tesla	$T = Wb/m^2$	-
Inductance	henry	$H = V\ s/A = Wb/A$	-
Complex Derived Units			
Angular Velocity	radian per second	rad/s	1 rad/s = 0.159155 rev/s
			1 rev/s = 6.28319 rad/s
Acceleration	metre per square second	m/s^2	$1\ m/s^2 = 3.28084\ ft/s^2$
			$1\ ft/s^2 = 0.3048\ m/s^2$
Angular Acceleration	radian per square second	rad/s^2	-
Pressure	newton per square metre	$N/m^2 = Pa$	$1\ N/m^2 = 145.038 \times 10^{-6}\ lbf/in^2$
			$1\ lbf/in^2 = 6.89476 \times 10^3\ N/m^2$
	bar	$bar = 10^5\ N/m^2$	-
			$1\ in.\ Hg = 3386.39\ N/m^2$
Torque	newton metre	N m	1 N m = 0.737562 lbf ft
			1 lbf ft = 1.35582 N m
Surface Tension	newton per metre	N/m	1 N/m = 0.0685 lbf/ft
			1 lbf/ft = 14.5939 N/m
Dynamic Viscosity	newton second per square metre	$N\ s/m^2$	$1\ N\ s/m^2 = 0.0208854\ lbf\ s/ft^2$
			$1\ lbf\ s/ft^2 = 47.8803\ N\ s/m^2$
Kinematic Viscosity	square metre per second	m^2/s	$1\ m^2/s = 10.7639\ ft^2/s$
			$1\ ft^2/s = 0.0929\ m^2/s$
Thermal Conductivity	watt per metre kelvin	W/m K	-
Odd Units*			
Radioactivity	becquerel	Bq	$1\ Bq = 2.7027 \times 10^{-11}$ Ci
			$1\ Ci = 3.700 \times 10^{10}$ Bq
Absorbed Dose	gray	Gy	1 Gy = 100 rad
			1 rad = 0.01 Gy
Dose Equivalent	sievert	Sv	1 Sv = 100 rem
			1 rem = 0.01 Sv
Exposure	coulomb per kilogram	C/kg	1 C/kg = 3876 R
			$1\ R = 2.58 \times 10^{-4}$ C/kg
Rate of Leak (Vacuum Systems)	millibar litre per second	mb l/s	1 mb = 0.750062 torr
			1 torr = 1.33322 mb

*These terms are recognised terms within the metric system.